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(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: MAHLER, Barry, Asher; 104 Carter Way, Glen Mills, PA 19342-1258 (US). MILLER, Ralph, Newton; 39 Hillstream Road, Newark, DE 19711-2477 (US).

(74) Agents: BOYER, Michael, K. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(54) Title: PROCESS FOR SEPARATING PENTAFLUOROETHANE FROM A MIXTURE COMPRISING HALOGENATED HYDRO-CARBONS AND CHLOROPENTAFLUOROETHANE
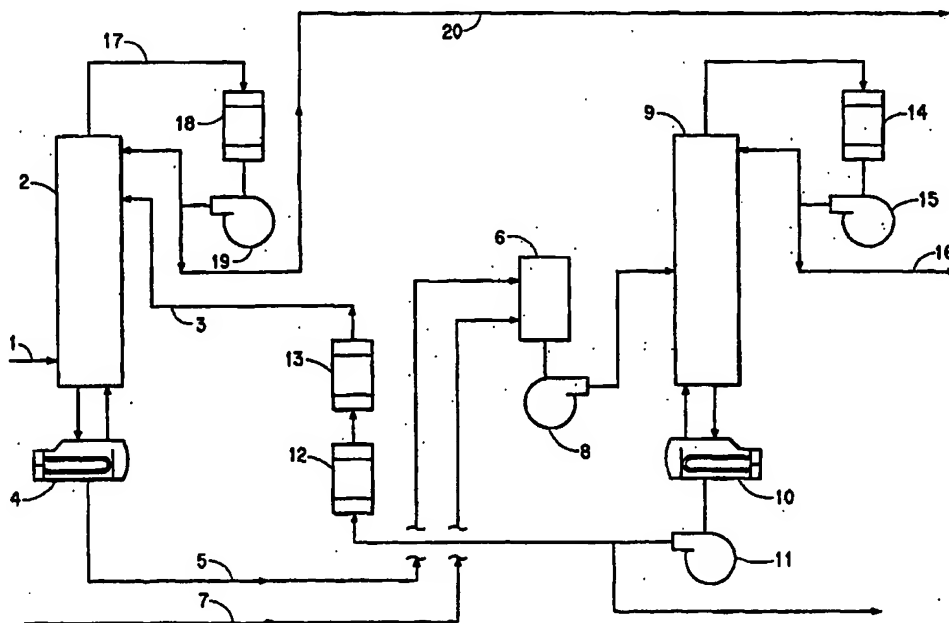
(57) Abstract

A process for separating pentafluoroethane from a mixture comprising pentafluoroethane and chloropentafluoroethane by employing extractive agents comprising a hydrochlorocarbon, hydrocarbon, chlorocarbons, among others.

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TITLE
Process for Separating Pentafluoroethane from a Mixture Comprising Halogenated Hydrocarbons and Chloropentafluoroethane

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FIELD OF THE INVENTION

The instant invention relates to a process for separating pentafluoroethane from a mixture comprising pentafluoroethane and chloropentafluoroethane by extractive distillation employing hydrocarbon, hydrochlorocarbon or

15   chlorocarbon extractive agents.

BACKGROUND OF THE INVENTION

New regulations have been designed to protect the stratospheric ozone layer from possible damage by fully halogenated chlorofluorocarbons.

20   Pentafluoroethane (CHF_2CF_3 or HFC-125) is a valuable non-chlorine containing fluorocarbon that is especially valuable as a refrigerant, blowing agent, propellant, fire extinguishing agent, sterilant carrier gas, among other uses.

Pentafluoroethane may be prepared by chlorofluorinating perchloroethylene (perclene or CCl_2CCl_2) to produce a mixture comprising

25   trichlorotrifluoroethane ($CF_2ClCFCl_2$ or CFC-113), dichlorotetrafluoroethane (CF_2ClCF_2Cl or CFC-114) and dichlorotrifluoroethane ($CFCl_2CHF_2$ or HCFC-123), and, after removing trichlorotrifluoroethane, fluorinating the remaining mixture to produce a mixture comprising pentafluoroethane (HFC-125), chloropentafluoroethane (CF_3CF_2Cl or CFC-115), and smaller amounts of other

30   fluorinated compounds, e.g., hexafluoroethane (CF_3CF_3 or FC-116). Such a chlorofluorinating method is described in U.S. Patent No. 3,755,477. Various other methods for making pentafluoroethane together with chloropentafluoroethane are known and are described, for example, in U.S. Patent Nos. 3,518,500, 3,258,500, Japanese Patent Application Publication Nos. JP 03/099026, JP 04/029941,

35   European Patent Application Publication No 0 506 525, and World Intellectual Property Organization Publication No. WO 91/05752. The disclosure of the previously identified patent documents is hereby incorporated by reference.

Whenever an extractive distillation process is employed for separating certain compounds, it is necessary to discover an extractive agent which will be

40   effective to sufficiently enhance the desired separation process. Methods which

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have been used to predict what extractive agents are likely to work have been described by L. Berg in Chem. Eng. Progress, Vol. 65, No. 9, pages 52-57, Sept. 1969; the disclosure of which is hereby incorporated by reference. When discussing extractive distillation, it was stated in the Berg article that "hydrogen bonds appear to be an important factor since all successful extractive distillation agents are highly hydrogen bonded liquids....Thus, the criteria for successful extractive agents are that they boil considerably higher than the compounds being separated, form no minimum azeotropes with the components, and be a highly hydrogen bonded liquid, that is, Class I or Class II of the hydrogen bond classification. Phenols, aromatic amines (aniline and its derivatives), higher alcohols, glycols, etc. are examples of successful extractive agents."

Extractive distillation agents that are capable of separating pentafluoroethane from chloropentafluoroethane are disclosed in US Patent No. 5,087,329 in which chlorofluorocarbons such as dichlorotetrafluoroethane (CFC-114) are employed. However, these CFC compounds are relatively expensive, and regulations concerning protection of the ozone layer will likely cause CFC compounds to be phased out as commercial products thereby making CFCs unavailable or uneconomic to use. The disclosure of U.S. Patent No. 5,087,329 is hereby incorporated by reference.

SUMMARY OF THE INVENTION

Conventionally used methods for manufacturing pentafluoroethane typically produce a mixture comprising pentafluoroethane (HFC-125) and chloropentafluoroethane (CFC-115). Such a mixture can form an azeotropic or azeotrope-like composition. The boiling points of pentafluoroethane and chloropentafluoroethane are relatively close, i.e., about -48.5 degrees C for pentafluoroethane and about -38.7 degrees C for chloropentafluoroethane, and their relative volatility is below about 1.1 at concentrations of pentafluoroethane greater than about 87.5 mole%, and below about 1.01 at concentrations greater than about 95 mole%. The above boiling points and relative volatilities indicate that it would be extremely difficult, if not impossible, to recover substantially pure pentafluoroethane from such a mixture by conventional distillation. By "conventional distillation", it is meant that the relative volatility only of the components of the mixture to be separated is being used to separate certain compounds. It was, therefore, surprising and unexpected that the instant invention can successfully employ not highly hydrogen bonded compounds as extractive

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distillation agents for separating pentafluoroethane from chloropentafluoroethane. By "extractive distillation" it is meant that a third component is added to the mixture to be separated so as to modify the relative volatilities of the compounds to be separated. By "not highly hydrogen bonded" it is meant that the extractive agent(s) are not characterized as being Class I or Class II of the hydrogen bond classification. The extractive distillation agents of the invention are also relatively inexpensive and readily available.

The instant invention solves the problems associated with conventional distillation methods by employing an extractive distillation process for separating pentafluoroethane from a first mixture comprising pentafluoroethane, chloropentafluoroethane and optionally hydrochlorofluorocarbons (HCFCs) such as HCFC-124, 124a, or hydrofluorocarbons such as HFC-143a, among others, which comprises:

(i) adding an extractant agent comprising at least one of a hydrocarbon such as pentane, hexane, heptane, octane, among others, and/or a hydrochlorocarbon such as triclene ($CHClCCl_2$), and/or a chlorocarbon such as perclene (CCl_2CCl_2), among others, to the first mixture in order to form a second mixture; wherein the extractant is a non-hydrogen bonder having two or more carbon atoms and an atmospheric boiling point greater than about 28 degrees C and less than about 126 degrees C,

(ii) separating pentafluoroethane from chloropentafluoroethane of the second mixture by extractively distilling the second mixture in an extractive distillation zone and thereby recovering as overhead product, a pentafluoroethane stream substantially free of chloropentafluoroethane.

The first mixture can be obtained from any suitable manufacturing process or source. For example, the first mixture can be obtained as product stream from the process disclosed in U.S. Patent Application Serial No. 07/989,481 that is a continuation of Serial No. 07/834,798 which in turn is a continuation in part of Serial No. 07/695,900, entitled "Process For The Manufacture of Pentafluoroethane" (corresponding to WIPO Publication No. WO 92/19576); the disclosure of which is hereby incorporated by reference.

The extractive agents used in the present invention are available from a number of suppliers at relatively low cost, and are much less expensive than fluorine-containing extractive agents, e.g., CFCs. The extractive agents of the instant invention can also be readily removed, for example, from the stream that exits from the bottom of the distillation column. The extractive agents can be

removed from the steam containing chloropentafluoroethane by simple distillation, and, if desired, reintroduced into the separation system.

Hydrocarbons that can be used as extractive agents are fluorine-free and comprise 5 to 8 carbon atoms. Specific examples of such hydrocarbons comprise or consist essentially of at least one member from group of normal or n-pentane, hexane, heptane, octane, their isomers and/or cyclic compounds thereof, among others, that possess an atmospheric boiling point from about 28 to about 126 C; normally about 28 to about 60° C. While hydrocarbons with higher boiling points and with more than 8 carbon atoms are also effective, such hydrocarbons are less desirable because they will typically require higher energy consumption, e.g., higher heat input.

Chlorocarbons (CCs) and hydrochlorocarbons (HCCs) that can be used as extractive agents comprise 2 carbon atoms and possess an atmospheric boiling point from about 74 to about 121° C. Specific examples comprise or consist essentially of at least one member from the group of perchloroethylene (perclene), methyl chloroform, 1,1 dichloroethane, 1,2 dichloroethane, trichloroethylene, ethylene dichloride, isomers and cyclic compounds thereof, among others. Higher boiling chlorocarbons and hydrochlorocarbons and those containing more than 2 carbon atoms are also effective, such compounds are less desirable because they will normally require higher energy consumption.

In one aspect of the invention, mixtures comprising or consisting essentially of the previously identified hydrocarbons, HCCs, and/or chlorocarbons can be employed as the extractive agent so long as the mixture has an atmospheric boiling point greater than about 28 degrees C.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1-Fig. 1 is a schematic diagram of an extractive distillation system which can be used for practicing the process of the invention.

DETAILED DESCRIPTION

The pentafluoroethane (HFC-125) and chloropentafluoroethane (CFC-115), which are the primary constituents of a first mixture, in their separated and pure state have boiling points, respectively, of about -48.5 and -38.7 degrees C. The relative volatility at atmospheric pressure of pentafluoroethane/chloropenta-fluoroethane was found to be nearly 1.0 as 100% purity of pentafluoroethane was

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5   approached. These data indicate that using conventional distillation procedures will not result in the separation of a substantially pure compound.

        To determine the relative volatility of pentafluoroethane and chloropentafluoroethane the so-called PTx Method is used. In this procedure, the total absolute pressure in a cell of known volume is measured at a constant

10   temperature for various known binary compositions. Use of the PTx Method is described in greater detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on pages 124 to 126; the entire disclosure of which is hereby incorporated by reference.

        These measurements can be correlated to equilibrium vapor and

15   liquid compositions in the cell by using an activity coefficient equation model, such as the Non-Random, Two-Liquid (NRTL) equation, to represent liquid phase non-idealities. Use of an activity coefficient equation, such as the NRTL equation, is described in greater detail in "The Properties of Gases and Liquids, 4th edition, publisher McGraw Hill, written by Reid, Prausnitz and Poling, on pages 241 to 387;

20   and in "Phase Equilibria in Chemical Engineering, published by Butterworth Publishers, 1985, written by Stanley M. Walas, pages 165 to 244; the entire disclosure of each of the previously identified references is hereby incorporated by reference.

        The result of PTx measurements and the above series of calculations

25   for a binary mixture containing HFC-125 and CFC-115 are summarized in Tables 1 through 3, giving results for -25 degrees C, 0 degrees C and 25 degrees C. Similar measurements were obtained and similar calculations were performed for the other binary combinations of compounds of the mixtures in the invention.

        Without wishing to be bound by any theory or explanation, it is

30   believed that the NRTL equation can sufficiently predict whether or not pentafluoroethane and chloropentafluoroethane mixtures and/or the following other mixtures behave in an ideal manner, and can sufficiently predict the relative volatilities of the components in such mixtures.

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Table 1

Vapor-Liquid Measurements on the HFC-125/CFC-115 System at -25 deg. C

Mole % CFC-115			Pressure	Relative Volatility
Charge	Liquid	Vapor	Meas. (psia)	HFC-125/CFC-115
17.67	17.72	15.85	40.75	1.144
13.48	13.51	12.38	40.75	1.105
10.40	10.42	9.74	40.95	1.078
7.40	7.42	7.08	41.10	1.052

Table 2

Vapor-Liquid Measurements on the HFC-125/CFC-115 System at 0 deg. C

Mole % CFC-115			Pressure	Relative Volatility
Charge	Liquid	Vapor	Meas. (psia)	HFC-125/CFC-115
17.67	17.78	15.92	96.95	1.142
13.48	13.55	12.37	97.20	1.110
10.40	10.45	9.69	98.00	1.087
7.40	7.43	7.00	98.00	1.066

Table 3

Vapor-Liquid Measurements on the HFC-125/CFC-115 System at 25 deg. C

Mole % CFC-115			Pressure	Relative Volatility
Charge	Liquid	Vapor	Meas. (psia)	HFC-125/CFC-115
17.67	17.87	16.36	198.60	1.113
13.48	13.61	12.65	200.25	1.087
10.40	10.49	9.88	200.75	1.069
7.40	7.45	7.11	201.00	1.052

The "Charge" column refers to the quantity of CFC-115 that is in a mixture of HFC-125 and CFC-115 that was introduced into the PTx cell. The "Relative/Volatility" and the Mole % CFC-115 in the Vapor and Liquid were those calculated from the Pressure measured at the temperature indicated on the above Tables.

      While the relative volatility of CFC-115 in comparison to HFC-125 at relatively low concentrations is sufficient to permit separating CFC-115 by using conventional distillation methods, the relative volatility is nearly 1.0 as 100% purity of HFC-125 as approached. A relative volatility approaching 1.0 would render removal of low concentrations of CFC-115 from HFC-125 by using conventional distillation difficult if not impossible, e.g., conventional distillation would require using large and expensive distillation columns.

      Using the equations developed for the above system at temperatures of about -25, 0 and about 25 degrees C, and when extrapolating to about -50 degrees C and a pressure of about 10 to about 20 psia, the presence of a low-boiling azeotropic or azeotrope-like mixture is indicated, with a composition of about 10 mole % CFC-115 and 90 mole % HFC-125. The existence of such a mixture is described in greater detail in copending and commonly assigned U.S. Patent Application Serial No. 08/055,486, filed on April 30, 1993 in the name of Mahler et al., and entitled "Process For Separating HCl And Halocarbons"; the disclosure of which is incorporated by reference. For best results, the inventive process herein avoids using conditions that cause formation of the HFC-125/CFC-115 azeotropic or azeotrope-like compositions.

      The problems associated with conventional distillation methods are overcome in the present invention by using an extractive distillation method. Extractive distillation depends upon the ability of certain extractive agents to increase the relative volatility of the binary pair of compounds to be separated. Extractive distillation is typically performed by operating a continuous distillation column, which comprises a multi-stage distillation column, with a minimum of two feed points, e.g. introducing the extractive agent at a first feed point which is located above the second feed point that is used for introducing the mixture to be separated, a reboiler and an overhead condenser for returning reflux to the column.

      Given the relative volatilities of pentafluoroethane and chloropentafluoroethane, it was a surprising and an unexpected result that they can be purified by extractive distillation using certain readily available and low cost non-fluorine containing compounds that are not highly hydrogen bonded and, in some cases, fluorine-free, e.g., hydrocarbons. The invention process can produce a purified HFC-125 product that is substantially free of CFC-115. By "substantially free" it is meant that the HFC-125 contains less than about 1.0 wt. % CFC-115, normally less than about .05 wt%, and in some cases less than about 10 ppm by weight CFC-115.

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In one aspect of the invention, an extractive agent, e.g. normal heptane, is introduced at an upper feed point of the distillation column, whereas the mixture requiring separation, e.g. pentafluoroethane and chloropentafluoroethane, is introduced at a relatively lower point in the column. The liquid extractive agent passes downwardly through trays which are located in the center of the column. While in the presence of the extractive agent, pentafluoroethane is relatively more volatile than chloropentafluoroethane, thereby allowing pentafluoroethane which is substantially free of chloropentafluoroethane to exit the top of the column, where the pentafluoroethane many be condensed by using conventional reflux condensers. At least a portion of this condensed stream can be returned to the top of the column as reflux, and the remainder recovered as a useful product. If desired the exiting pentafluoroethane can be recycled to the column or a second column for further purification.

The chloropentafluoroethane and an extractive agent exiting the bottom of the column can then be passed to a stripper or distillation column for separation by using conventional distillation or other known methods. If desired, the extractive agent may then be recycled to the extractive distillation column. In some cases, the CFC-115 can be separated from the remaining constituents of the stream by using conventional distillation or other known methods.

The ratio of the material exiting the top of the column, which is then condensed and in turn returned to the column, to the amount of material which is removed as product is commonly referred to as the reflux ratio. The reflux ratio will define the physical characteristics of the distillation column. In general, an increase in the reflux ratio will in turn cause an increase in the purity of the recovered HFC-125, e.g., the quantity of extractant in the recovered HFC-125 can be reduced. Increasing the reflux ratio typically requires employing larger and more expensive distillation column.

The specific conditions which can be used for practicing the invention are interrelated and depend upon a number of design parameters such as the diameter of the column, selected feed points, the number of separation stages in the column, reflux ratio, among others. The operating pressure of the distillation system may range from about 15 to 350 psia, normally about 50 to 300 psia. Typically, an increase in the extractant feed rate relative to the mixture to be separated will result in an increase in the purity of the pentafluoroethane produced. The temperature and heat transfer area of the overhead condenser is normally sufficient to

substantially fully condense the pentafluoroethane, or is optionally sufficient to achieve the desired reflux ratio by partial condensation.

The temperature that is employed at a given step in the inventive process is a function of the pressure and the design characteristics of the distillation column, e.g., the ratio of extractive agent to the first mixture. Typically, the temperature will range from about -25 to 200°C based upon an operating pressure of about 200 psia.

The quantity of CFC-115 in the first mixture, i.e., the HFC-125-containing mixture to be purified, can be reduced by using conventional distillation. While conventional distillation methods are incapable of producing HFC-125 that is substantially free of CFC-115, conventional distillation can be used for reducing the initial quantity of CFC-115 in the first mixture. For example, conventional distillation can be used for removing relatively large or bulk quantities of CFC-115 from HFC-125, which in turn is processed in accordance with the invention method, in order to obtain a substantially CFC-115-free HFC-125 product. Depending upon the quantity of HFC-125 in the first mixture, HFC-125 can be removed from a mixture containing relatively large quantities of CFC-115 thereby producing CFC-115 that is substantially free of HFC-125.

The effective amount of the extractive agent(s) can vary widely. In general, however, using an increased amount of extractive agent will enhance the purity of the recovered HFC-125, e.g., the removal rate of CFC-115 is increased. Typically, the ratio of extractive agent to HFC-125 ranges from about 2 to about 3:1 on a weight basis. But higher ratios may be necessary for the more difficult separations.

Referring now to the Figure, Fig. 1 schematically illustrates a system which can be used for operating the inventive distillation process. A first mixture comprising pentafluoroethane and chloropentafluoroethane is supplied via conduit 1 to extraction column 2. At least one liquid extractive agent is supplied via conduit 3 to the extraction column 2, and introduced into column 2 at a location above the mixture 1. A second mixture comprising extractive agent(s), chloropentafluoro-ethane and other impurities, is removed from the bottom of column 2 and transported to steam-heated reboiler 4. In some cases, the reboiler 4 is attached to the extractive column 2. The second mixture is supplied via conduit 5 to a feed tank 6. Supplemental liquid extractive agent is also supplied to feed tank 6 via conduit 7 thereby forming a third mixture or extraction agent recycle. A pump 8 transports the third mixture to a stripping column 9. Stripping column 9 separates the

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extractive agent from non-extractive agents. Extractive agent is removed from column 9 and supplied to a second steam heated reboiler 10. In some cases, the reboiler 10 is attached to column 9. Pump 11 transports the extractive agent from the reboiler 10 through a cold water chiller 12, and then to chiller 13. If necessary, excess quantities of extraction agent can be purged prior to reaching chiller 12. Typically, chiller 13 is operated at a temperature of about -25° C. After exiting chiller 13, the extraction agent is supplied via conduit 3 into extraction column 2.

CFC-115 exits from the top of stripping column 9 as an off gas, and are introduced into condenser 14, which is typically operated at a temperature of about -25° C. While under reflux conditions, pump 15 returns a portion of the CFC-115 to the stripping column 9. The remaining portion of the CFC-115 exits the system via conduit 16.

An off gas is also removed from extraction column 2, with the exception that the off gas from column 2 contains HFC-125 product which is substantially free from CFC-115 of the first mixture. The HFC-125 product is transported via conduit 17 to condenser 18. Condenser 18 is typically operated at a temperature of about -25° C. While under reflux conditions, pump 19 returns a portion of the HFC-125 product to extraction column 2. The HFC-125 product exits the system via conduit 20.

The following examples are provided to illustrate certain aspects of the present invention; but not limit the scope of the invention as defined by the appended claims. Parts per million (ppm) concentrations are by weight unless otherwise specified. The following Examples employ the NRTL interaction parameters identified above. All Examples are based upon a feed rate of pentafluoroethane of about 1000 lb/hr, with the impurity content of chloropenta-fluoroethane at a level of either approximately 5 lb/hr (4975 ppm) or 50 lb/hr (4.8%). A different column design and operating conditions are used for the Examples in which extractive distillation is employed than those in which conventional distillation is employed, in order to enhance the performance of each distillation method.

In the following Comparative Examples involving conventional distillation, the number of stages in the distillation column is either 101 or 121 stages, and the pentafluoroethane stream to be purified is fed onto column stage 50, with the column condenser corresponding to stage no.1. Depending upon the desired product purity, the operating conditions are selected and various reflux ratios tested to maximize the yield of such a product.

Comparative Example 1

In this comparative example, conventional distillation is used in a column with 121 theoretical stages for purifying a feed stream containing 1000 lb/hr of pentafluoroethane (HFC-125) and 5 lb/hr of chloropentafluoroethane (CFC-115), for a concentration of 4975 ppm. The feed is introduced at a temperature of -25 degrees C, with the column condenser pressure at 194.7 psia and the column base pressure 3 psi higher. The distillate temperature is 23.8 degrees C, and the bottom column temperature is 24.4 degrees C. Under these operating conditions, the product HFC-125 will leave in the overhead (distillate) stream from the column. The remaining HFC-125 exits in the bottoms stream with CFC-115 as a waste product. Conditions are set so that about 50% of the feed goes into the overhead and 50% to the bottoms.

Table 4

Reflux Flow (lb/hr)	Reflux Ratio	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	% HFC-125 Recovery
100000	200/1	501	2116	50
200000	400/1	501	1936	50
300000	600/1	501	1871	50

The product purity is relatively low, even with a relatively high reflux ratio of 600/1 and a large number of theoretical separation stages in the column.

Comparative Example 2

In this comparative example, conventional distillation is used in a column with 101 theoretical stages for purifying a feed stream of the same composition as Comparative Example 1. The operating conditions of the distillation column are modified to employ the CFC-115/HFC-125 azeotrope, discussed above that exists at very low temperatures, by taking the azeotrope overhead as a means of removing the CFC-115 in the feed. The feed is introduced at a temperature of -25 degrees C, with the column condenser pressure set at 19.7 psia and the column base pressure 3 psi higher. Under these conditions the distillate temperature is -42 degrees C, and the bottom column temperature is -38.8 degrees C. Under these operating conditions, the product HFC-125 leaves in the bottom stream from the

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column. An impurity level of 500 ppm CFC-115 is selected. The remaining HFC-125 is taken overhead with azeotroped CFC-115 as a waste product.

Table 5

Reflux flow (lb/hr)	Reflux Ratio	Lb/hr HFC-125 in Bottoms	ppm CFC-115 in Bottoms	% HFC-125 Recovery
10000	21/1	529	500	52.9
25000	329/1	930	500	93.0
50000	862/1	950	500	95.0
100000	1852/1	955	500	95.5

At a reflux ratio of 1852/1, and with the impurity level of 500 ppm CFC-115, the yield of HFC-125 product is 95.5%.

Comparative Example 3

In this comparative example, conditions are the same as Comparative Example 2 except that product purity requirement is increased: that is, the maximum allowed level of CFC-115 impurity is reduced from 500 to 50 ppm.

Table 6

Reflux flow (lb/hr)	Reflux Ratio	Lb/hr HFC-125 in Bottoms	ppm CFC-115 in Bottoms	% HFC-125 Recovery
50000	115/1	565	50	56.5
100000	585/1	832	50	83.2
150000	1083/1	865	50	86.5

At a reflux ratio of 1083/1, about 15% of the HFC-125 in the feed is lost with the distillate.

The above Examples show that conventional distillation is not an economical way to separate CFC-115 from HFC-125 when high purity HFC-125 is desired because such require a relatively high reflux ratio, a large column diameter to accommodate this high reflux ratio, high utilities cost for heating and cooling this large flow of material through the column, and the need for disposing of large

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5   quantities of waste material containing CFC-115. Such waste material will also
       contain a relatively large quantity of HFC-125.

                 In the following Examples involving extractive distillation, which are
       provided to illustrate; but not limit the scope of the invention, the distillation
       column has only 57 theoretical stages, again with the column condenser counted as
10   stage no. 1. The pentafluoroethane stream to be purified is introduced onto column
       stage 40, and the extractant is fed onto column stage 15. In each Example, the
       column distillate/feed ratio (based on pentafluoroethane) and the reflux ratio are
       set to achieve the desired product purity and recovery (yield), and operating
       temperatures and pressures are varied as necessary to maximize operating
15   conditions. Except for Example 2, column pressures are selected so that the
       bottoms temperature is approximately 100 degrees C. Each of the Examples also
       includes a measurement of performance at varied levels of extractant flow rates.

                                        Example 1

20   In this example, extractive distillation with normal pentane is used in
       a column with 57 theoretical stages for purifying a feed stream containing 1000
       lb/hr of pentafluoroethane (HFC-125) and 5 lb/hr of chloropentafluoroethane
       (CFC-115) or 4975 ppm as in the Comparative Examples. The feed and extractant
       are introduced at a temperature of -5 degrees C, with the column condenser
25   pressure set at 84.7 psia and the column base pressure 3 psi higher. The normal
       pentane is fed at varying rates as shown in the table, while the reflux ratio is held at
       only 3/1. The distillate temperature is -4.4 degrees C, and the bottom column
       temperature is about 100 degrees C. The pentane and most of the CFC-115 leave
       the bottom of the column, and the product HFC-125 leaves the top of the column as
30   overhead.

                                        Table 7

Lb/hr Pentane Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
2500	999	911	5.8	99.9
5000	999	73	6.1	99.9
7500	999	12	6.3	99.9
10000	999	3.3	6.5	99.9

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Example 2

Example 2 is carried out in substantially the same way as Example 1 except that the column condenser pressure is 34.7 psia instead of 84.7 psia, and the feed and pentane are introduced at a temperature of -25 degrees C, with the column condenser pressure set at 34.7 psia and the column base pressure 3 psi higher. The distillate temperature is -29 degrees C, and the bottom column temperature is about 66 degrees C.

Table 8

Lb/hr Pentane Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
2500	999	1720	<0.1	99.9
5000	999	148	<0.1	99.9
7500	999	21	<0.1	99.9
10000	999	5.0	<0.1	99.9

In both Examples 1 and 2, extractive distillation with pentane permits a relatively high purity HFC-125 product to be obtained at high product yield, while using a relatively small distillation column and reflux ratio.

Example 3

Example 3 is carried out in substantially the same way as Example 1 except that the impure HFC-125 feed contains ten times as much CFC-115, i.e. a flow rate of 50 lb/hr instead of 5 lb/hr, for a concentration of 4.8%. The distillate temperature is -4.4 degrees C, and the bottom column temperature ranges from 95 to 100 degrees C, depending on the flow rate of pentane.

Table 9

Lb/hr Pentane Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
2500	999	4175	5.6	99.9
5000	999	431	6.1	99.9
7500	999	81	6.3	99.9
10000	999	24	6.4	99.9

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Table 9 (cont.)

Lb/hr Pentane Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
15000	999	4.9	6.6	99.9
20000	999	1.8	6.8	99.9

This demonstrates that using pentane as an extractive agent permits obtaining high purity HFC-125 from a mixture having an impurity concentration of about ten times greater than in the Comparative Examples.

Example 4

Example 4 is carried out in substantially the same way as Example 1 except that the extractant is cyclopentane and the column pressure is 54.7 psia. The distillate temperature is -17 degrees C, and the bottom column temperature ranges from 94 to 98 degrees C, depending on the flow rate of extractant.

Table 10

Lb/hr Extract. Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
1000	999	918	<0.01	99.9
1500	999	168	<0.01	99.9
2500	999	11	<0.01	99.9
5000	999	0.2	<0.01	99.9
7500	999	<0.1	<0.01	99.9

Example 5

Example 5 is carried out in substantially the same way as Example 2 except that the extractant is normal hexane. The distillate temperature is -29 degrees C, and the bottom column temperature ranges from 101 to 102 degrees C, depending on the flow rate of extractant.

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Table 10

Lb/hr Hexane Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
2500	999	41	<0.01	99.9
5000	999	0.9	<0.01	99.9
7500	999	0.1	<0.01	99.9
10000	999	0.02	<0.01	99.9

Example 6

Example 6 is carried out in substantially the same way as Example 5 except that the reflux ratio is reduced from 3/1 to 1/1.

Table 11

Lb/hr Hexane Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
2500	999	217	<0.01	99.9
5000	999	4.2	<0.01	99.9
7500	999	0.3	<0.01	99.9
10000	999	0.04	<0.01	99.9

Example 7

Example 7 is carried out in substantially the same way as Example 2 except that the extractant is normal heptane, the column condenser pressure is 12.7 psia, and the feed and extractant are introduced at a temperature of -40 degrees C. The distillate temperature is -51 degrees C, and the bottom column temperature ranges from 97 to 100 degrees C, depending on the flow rate of extractant.

Table 12

Lb/hr Heptane Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
2500	999	307	<0.01	99.9
5000	999	6.9	<0.01	99.9
7500	999	0.67	<0.01	99.9
10000	999	0.14	<0.01	99.9

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Example 8

Example 8 is carried out in substantially the same way as Example 2 except that the extractant is perchloroethylene (perclene), the column condenser pressure is 4.7 psia, and the feed and extractant are introduced at a temperature of -40 degrees C. The distillate temperature is -69 degrees C, and the bottom column temperature ranges from 93 to 98 degrees C, depending on the flow rate of extractant.

Table 13

Lb/hr Perclene Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
5000	999	3586	<0.01	99.9
10000	999	695	<0.01	99.9
20000	999	436	<0.01	99.9
30000	999	533	<0.01	99.9
40000	999	411	<0.01	99.9
50000	999	245	<0.01	99.9

Example 9

Example 9 is carried out in substantially the same way as Example 2 except that the extractant is trichloroethylene (triclene), the column condenser pressure is 18.7 psia, and the feed and extractant are introduced at a temperature of -40 degrees C. The distillate temperature is -43 degrees C, and the bottom column temperature ranges from 99 to 100 degrees C, depending on the flow rate of extractant.

Table 14

Lb/hr Triclene Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
5000	999	4680	<0.01	99.9
10000	999	3014	<0.01	99.9
20000	999	782	<0.01	99.9
30000	999	251	<0.01	99.9

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5	40000	999	106	<0.01	99.9
	50000	999	55	<0.01	99.9

Example 10

Example 10 is carried out in substantially the same way as Example 1 except that the extractant is a mixture of 50% by weight normal pentane and 50% hexane, the column condenser pressure is 64.7 psia, and the feed and extractant are introduced at a temperature of -10 degrees C. The distillate temperature is -12 degrees C, and the bottom column temperature ranges from 103 to 104 degrees C, depending on the flow rate of extractant.

Table 15

Lb/hr Extract. Feed Rate	Lb/hr HFC-125 in Overhead	ppm CFC-115 in Overhead	ppm Extractant in Overhead	% HFC-125 Recovery
2500	999	200	0.8	99.9
5000	999	7.8	0.9	99.9
7500	999	1.1	0.9	99.9
10000	999	0.3	1.0	99.9

This Example illustrates that a mixed extractant may be effectively used for in the inventive process. In some cases, such mixtures may be available at a much lower price than pure materials. For example, by using a mixture of extractant agents the inventive process can be maximized to obtain HFC-125 that has the desired purity while minimizing the extractive agent cost. Alternatively, a series of one or more chemically similar or distinct extractive agents can be employed for maximizing the effectiveness of the inventive process.

While certain aspects of the invention have been described in particular detail, a person in this art would understand that other embodiments and variations are covered by the appended claims.

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THE FOLLOWING IS CLAIMED:

1. A process for separating pentafluoroethane from a first mixture comprising chloropentafluoroethane and pentafluoroethane, the process comprising the steps of:

adding at least one of a hydrocarbon, chlorocarbon and hydrochlorocarbon extractive agent to the first mixture in order to form a second mixture, wherein the hydrocarbon extractant agent has at least five carbon atoms and the chlorocarbon or hydrochlorocarbon extractant has at least two carbon atoms; and wherein the extractant agent has an atmospheric boiling point greater than about 28 degrees C,

separating the chloropentafluoroethane from the pentafluoroethane of the second mixture by extractively distilling the second mixture in an extractive distillation zone, and;

recovering pentafluoroethane substantially free of chloropentafluoroethane.

2. The process of Claim 1 wherein the extractive agent comprises at least one hydrocarbon containing 5 to 8 carbons, their isomers and cyclic compounds thereof having an atmospheric boiling point greater than about 28 degrees C and less than about 126 degrees C.

3. The process of Claim 1 wherein the extractive agent comprises at least one chlorocarbon and hydrochlorocarbon containing 2 carbon atoms, their isomers and cyclic compounds having an atmospheric boiling point greater than about 28 degrees C and less than about 126 degrees C.

4. The process of Claim 1 wherein the extractive agent comprises at least one member selected from the group consisting of perchloroethylene, methyl chloroform, 1,1 dichloroethane, 1,2 dichloroethane, trichloroethylene, and ethylene dichloride.

5. The process of Claim 1 wherein the extractive agent comprises at least one member selected from the group consisting of n-pentane, hexane, heptane, octane, their isomers and cyclic compounds thereof having an atmospheric boiling point greater than about 28 degrees C and less than about 126 degrees C.

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6. A process for separating chloropentachloroethane from a first mixture comprising chloropentafluoroethane and pentafluoroethane, the process comprising the steps of:

adding at least one extractive agent to the first mixture in order to form a second mixture, wherein the extractant agent is fluorine free and does not hydrogen bonds; and wherein the extractant agent has an atmospheric boiling point greater than about 28 degrees C,

separating the chloropentafluoroethane from the pentafluoroethane of the second mixture by extractively distilling the second mixture in an extractive distillation zone, and;

recovering pentafluoroethane.

7. A process for separating chloropentachloroethane from a first mixture comprising chloropentafluoroethane and pentafluoroethane, the process comprising the steps of:

adding at least one extractive agent to the first mixture in order to form a second mixture, wherein the extractant agent is fluorine free and does not hydrogen bond; and wherein the extractive agent has at least two carbon atoms; and wherein the extractant agent has an atmospheric boiling point greater than about 28 degrees C,

separating the chloropentafluoroethane from the pentafluoroethane of the second mixture by extractively distilling the second mixture in an extractive distillation zone, and;
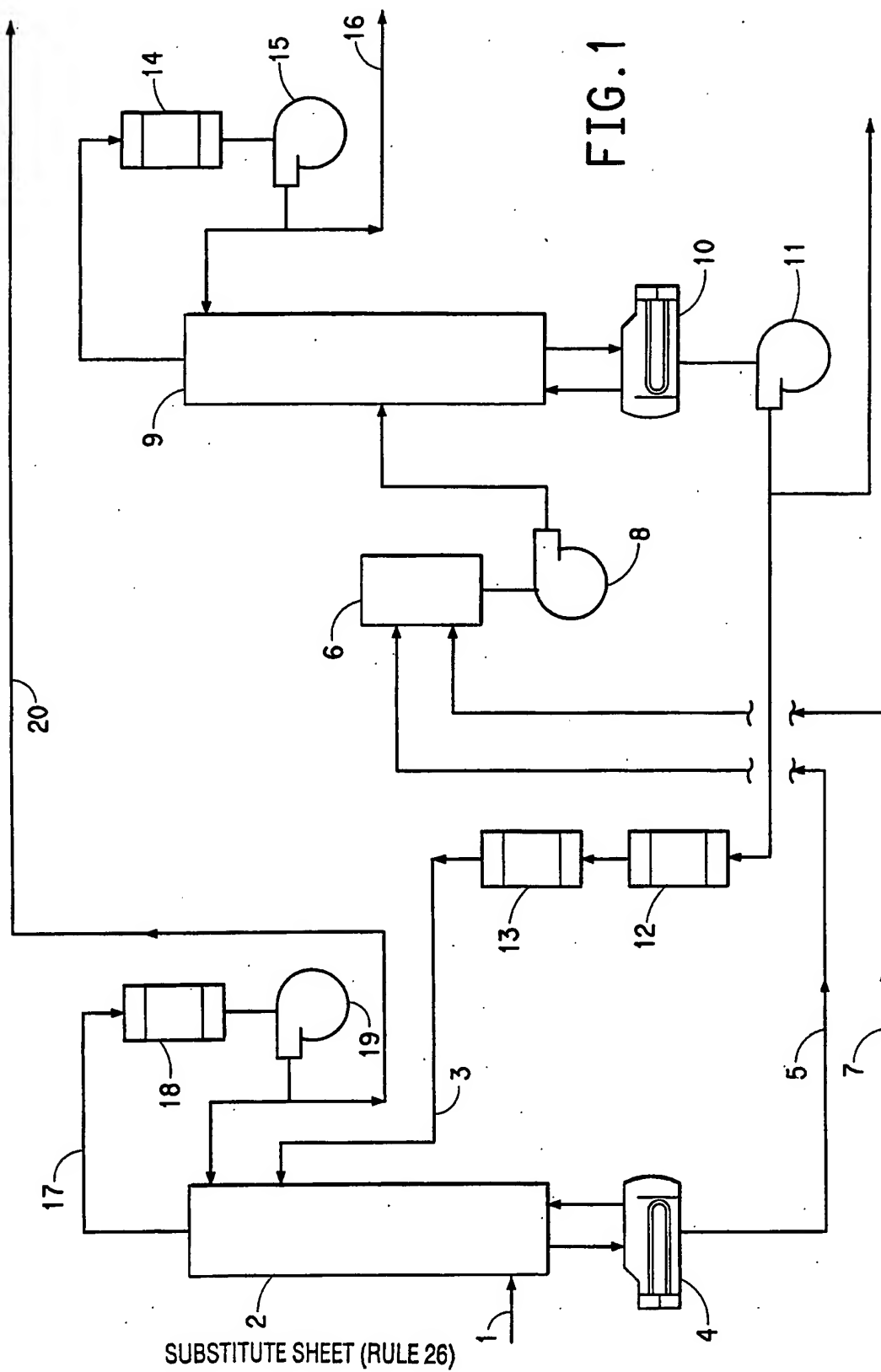
recovering pentafluoroethane.

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FIG.1

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C17/386   C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 626 362 (SHOWA DENKO KABUSHIKI KAISHA) 30 November 1994 see the whole document ---	1,2,5-7
P,X	RESEARCH DISCLOSURE, vol. 360, 1994 EMSWORTH GB, pages 191-193, 'Methods for Separating Chloro-Carbons from Hydrofluoroalkanes' see the whole document ---	1-5
Y	US,A,5 087 329 (V.M. FELIX) 11 February 1992 cited in the application see the whole document ---	1-5
Y	EP,A,0 472 391 (IMPERIAL CHEMICAL INDUSTRIES PLC) 26 February 1992 see the whole document ---	1-5

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|X| Further documents are listed in the continuation of box C. |X| Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 May 1995	

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 564 036 (SOLVAY (SOCIÉTÉ ANONYME)) 6 October 1993 see the whole document -----	1-5

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-626362	30-11-94	AU-B-	6328394	01-12-94
		BR-A-	9402038	07-03-95
		CA-A-	2124282	26-11-94
US-A-5087329	11-02-92	AU-A-	8735591	30-12-92
		BR-A-	9107306	28-06-94
		CA-A-	2103279	17-11-92
		CN-A-	1066647	02-12-92
		EP-A-	0584070	02-03-94
		JP-T-	6510980	08-12-94
		WO-A-	9220640	26-11-92
EP-A-472391	26-02-92	JP-A-	4257533	11-09-92
		US-A-	5200431	06-04-93
EP-A-564036	06-10-93	FR-A-	2689503	08-10-93
		JP-A-	6009449	18-01-94
		US-A-	5306850	26-04-94